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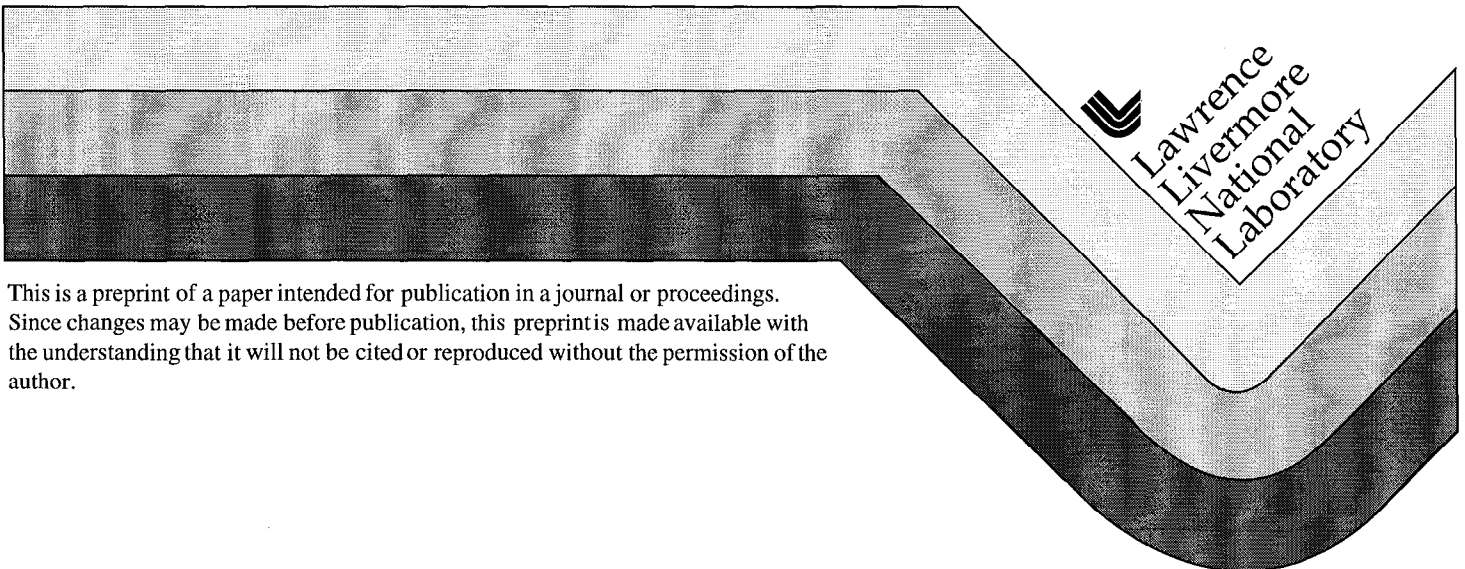
PREPRINT

Experimental Investigation of Beryllium-Based Multilayer Coatings for Extreme Ultraviolet Lithography

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Experimental investigation of beryllium-based multilayer coatings for extreme ultraviolet lithography

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ABSTRACT

The performance of beryllium-based multilayer coatings designed to reflect light of wavelengths near 11 nm, at normal incidence, is presented. These multilayer coatings are of special interest for extreme ultraviolet lithography (EUVL). The beryllium-based multilayers investigated were Mo/Be, Ru/Be and a new material combination Mo₂C/Be. The highest reflectivity achieved so far is 70% at 11.3 nm with 70 bilayers of Mo/Be. However, even though high reflectivity is very important, there are other parameters to satisfy the requirements for an EUVL production tool. Multilayer stress, thermal stability, radiation stability and long term reflectance stability are of equal or greater importance. An experimental characterization of several coatings was carried out to determine the reflectivity, stress, microstructure, and long term stability of these coatings. Theoretically calculated reflectivities are compared with experimental results for different material pairs; differences between experimental and theoretical reflectivities and bandwidths are addressed.

Keywords: Extreme ultraviolet (EUV) lithography, reflective coatings, multilayer deposition, beryllium.

1. INTRODUCTION

Reflective multilayer coatings are one of the major enabling technologies of extreme-ultraviolet (EUV) lithography. Finding the coating which gives optimum optical and mechanical properties is crucial for the commercial success of EUVL. Beryllium has been traditionally used for x-ray windows at synchrotron beamlines and on x-ray detectors and bandpass windows in telescopes due to its high transparency. In recent years it has been possible to fabricate multilayer mirrors with beryllium as a spacer material.¹⁻⁵ There are many reasons why beryllium-based multilayers are attractive for EUV lithography. Beryllium-based multilayers have a high theoretical normal incidence reflectance at wavelengths above the Be absorption edge, leading to high throughput of an optical system. For example, the theoretical reflectivity of an ideal Mo/Be multilayer at near normal incidence angles is calculated to be around 76%.⁴ More importantly, the current Xe-cluster jet source is approximately five times brighter at 11.3 nm than at 13.4 nm,^{5,6} where the current Si-based multilayers operate. This plasma source has a maximum peak in EUV power at a wavelength of 10.9 nm.

Beryllium-based multilayer systems have not been studied as much as Mo/Si multilayers. This is mainly due to the fact that beryllium is a hazardous material in powder form so the safety requirements during the deposition are more stringent. Previous papers presented investigations of peak reflectance versus the number of bilayers and under various deposition conditions¹, or reported about the structural characterization of beryllium based multilayer coatings.² In addition to Mo/Be, some other beryllium based multilayer systems were examined, such as Nb/Be,¹ Ru/Be,² and Rh/Be.² Of all Be-

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based coatings previously investigated, the Mo/Be coatings consistently gave the best reflectance results and therefore were studied in more detail.

In this paper we report other properties of Mo/Be multilayers, such as intrinsic stress and stress stability with time, reflectance stability with time, reflectance stability at elevated temperatures and reflectance stability of multilayers exposed to EUV radiation. Furthermore, we examine in more detail different factors that contribute to the reflectance loss in the multilayers such as roughness, interlayer mixing and surface oxidation. Besides Mo/Be coatings we studied Ru/Be and Mo₂C/Be.

2. DEPOSITION SYSTEM AND PARAMETERS

The beryllium-based multilayers are deposited using a DC magnetron sputtering system (Fig. 1). The whole system is housed in an exhausted enclosure to prevent exposure of the operator to hazardous Be dust. The coating system consists of two large (12.7 x 25.4 cm) rectangular sputter sources, and two small circular sputter sources (10.1 cm diameter), all mounted on the bottom of the chamber. The substrate to be coated is mounted facing down on a platter, which rotates in one direction to expose the substrate to alternate sources. The platter velocity, which can be modulated, determines the thickness of the deposited layer. Substrates are rapidly spun around their center axis by a spinner assembly to improve uniformity of the deposition thickness across the substrate. Chimneys are used to prevent the deposition anywhere except directly above the sources. Only one pump is typically used during deposition. A typical base pressure is 5×10^{-8} Torr. Ultrahigh purity Ar at a pressure of 0.8-1.0 mTorr is used to sputter Mo, Ru, Be and Mo₂C targets at source powers of 50-360 W.

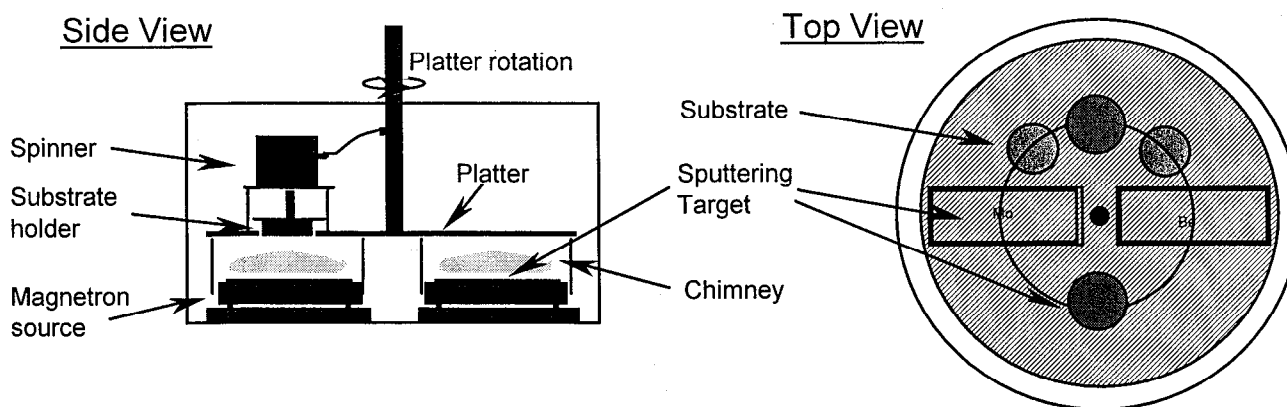


Figure 1: Side and top schematic view of the sputter deposition system.

In the EUV lithography system⁷ seven normal-incidence mirrors have to be spectrally matched with each other. Narrow reflectance peaks (0.5 nm for Mo/Si coatings) make this a very challenging job. The narrower the peak the greater the accuracy required in controlling the wavelength of the peak. For example, a 70-bilayer Mo/Be multilayer has a reflectance bandwidth of only 0.27-0.29 nm and the centroids of all reflectance peaks must match to 0.02 nm. This requires stringent thickness control of uniform and graded coatings.

3. RESULTS AND DISCUSSION

Three multilayer systems were studied: Mo/Be, Ru/Be and Mo₂C/Be. Our data suggest that the reflectance is mainly altered by the roughness, interlayer mixing and surface oxidation of the multilayers. The roughness itself is a function of the Ar pressure during the deposition, the degree of crystallinity of the materials and the substrate roughness as presented in the next section. We will compare the results for reflectance, intrinsic stress, reflectance and stress stability of all three systems whenever possible.

3.1 Reflectance

The measurements were made at 5° from normal incidence using a synchrotron-based EUV reflectometer attached to beamline 6.3.2 at the Advanced Light Source.⁸ The highest reflectance mirror we have made was a Mo/Be mirror with 70.2% reflectance at 11.34 nm and bandwidth of 0.27 nm (Fig. 2). This Mo/Be multilayer consists of 70 bilayers with a bilayer thickness of 5.7 nm. Theoretical calculations using updated values for the atomic scattering factors of Be demonstrated that, ideally, Mo/Be optics can have reflectivity of about 75% over an energy range extending from 95 eV up to the Be K-edge (111.5 eV). Our experimental mirrors achieved over 92% of the theoretical reflectivity value.⁹

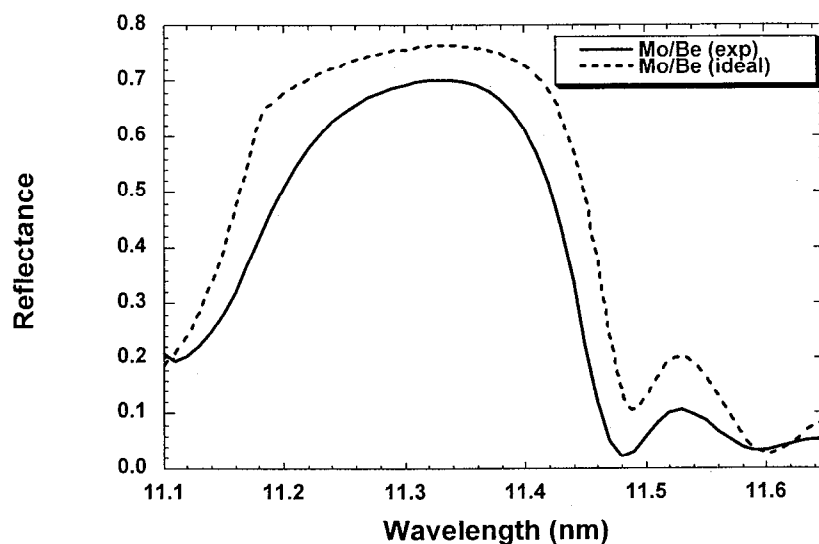


Figure 2: Theoretical (dotted) and experimental (solid) reflectance curves of Mo/Be multilayer. The kink in the theoretical (ideal) curve at around 11.17 nm is due to the Be absorption edge.

The highest reflectance in Ru/Be multilayer coatings was achieved with 50 bilayers and a bilayer thickness of 5.87 nm. A plot of the reflectivity as a function of wavelength is given in Fig. 3. The measured reflectance was 63.7% at 11.4 nm and the bandwidth was 0.34 nm. The ideal Ru/Be multilayer should have a reflectivity of 77% and 0.45 nm bandwidth. In this multilayer we achieved 82% of the maximum theoretical reflectance.

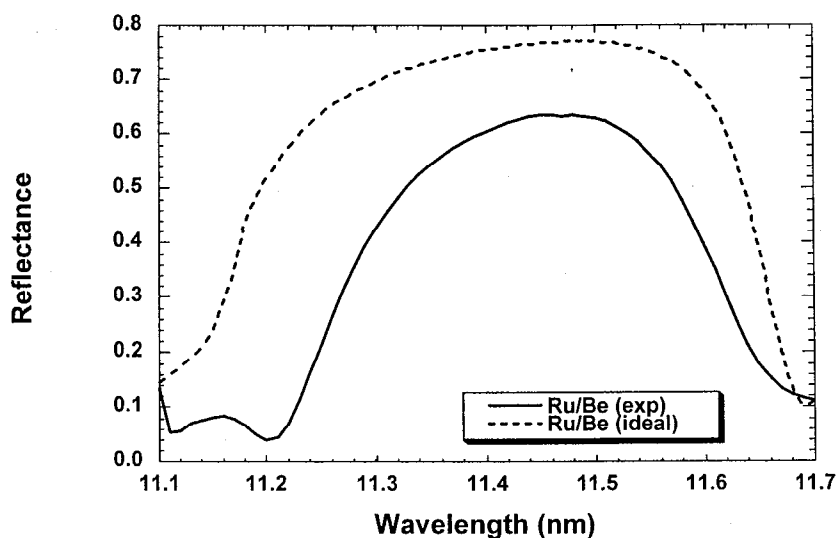


Figure 3: Theoretical and experimental reflectance curve of Ru/Be multilayer.

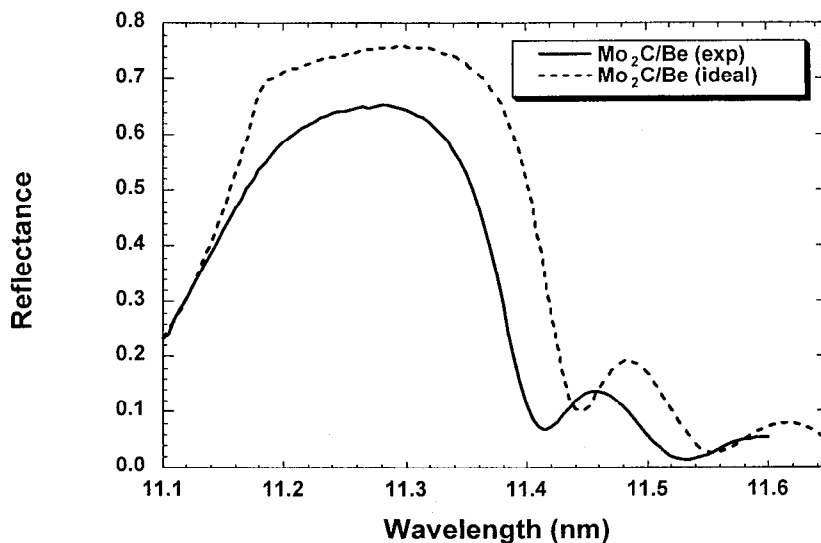


Figure 4: Theoretical and experimental reflectance curve of Mo₂C/Be multilayer.

The best reflectance of the third multilayer system, Mo₂C/Be, was 65.3% at 11.25 nm with a bandwidth of 0.25 nm (Fig. 4). This is 87% of the maximum theoretical reflectance (75%). The measured reflectance peak was narrower than the theoretically calculated one, i.e. 0.25 nm instead of 0.29 nm.

In all three cases we achieved above 80% of the maximum theoretical reflectance which suggests high quality multilayers. Additional analyses were performed to determine the cause of the discrepancy between the theoretical and the experimental results.

3.1.1. Roughness

The reflectance of Mo/Be multilayer mirrors was initially maximized by optimizing the power of the sputtering sources and the argon sputtering pressure. A highest reflectance of 70% was achieved. The highest reflectance was obtained at an Ar pressure of 0.84 mTorr, which is the lowest pressure at which the Be and the Mo sputter sources are stable.

The TEM, which is an invaluable technique to study the microstructure of the multilayers, was used to view the multilayers in cross section. The high resolution TEM work was done on a JEOL 4000EX operating at 400keV at Sandia National Laboratory in Livermore. The samples were prepared by a process which included: (i) gluing several pieces together, face-to-face and potting a cored sectioned from the laminated pieces in a 3 mm diameter tube with epoxy, (ii) slicing a disc from the tube, (iii) lapping it to 100μm followed by (iv) dimpling to 10μm then (v) low angle ion milling to electron transparency.

High-resolution transmission electron microscopy (TEM) cross section images of Mo/Be multilayers (Figs. 5(a)-(c)) show the effect of Ar sputtering pressure on the roughness of the multilayers. The deposition runs were done at Ar pressures of 2.5, 1.7 and 0.8 mTorr. The roughness of the layers increases with the increasing pressure. The energy of the sputtered atoms decreases with increasing pressure and the reduced mobility of the atoms could result in a columnar growth and increased roughness as shown in Figs. 5(a)-(c). This high frequency roughness decreases the measured reflectivity by scattering EUV light outside the typical field of view.

For the three multilayer systems under study we determined the optimal deposition parameters by varying the bilayer thickness, thickness ratio (thickness of the high Z material divided by the bilayer thickness), and the source power. Theoretical modeling predicts that a larger number of bilayers should give higher reflectivity. However, the theoretical model does not take into account that the roughness of the multilayer coating increases with the number of bilayers, as

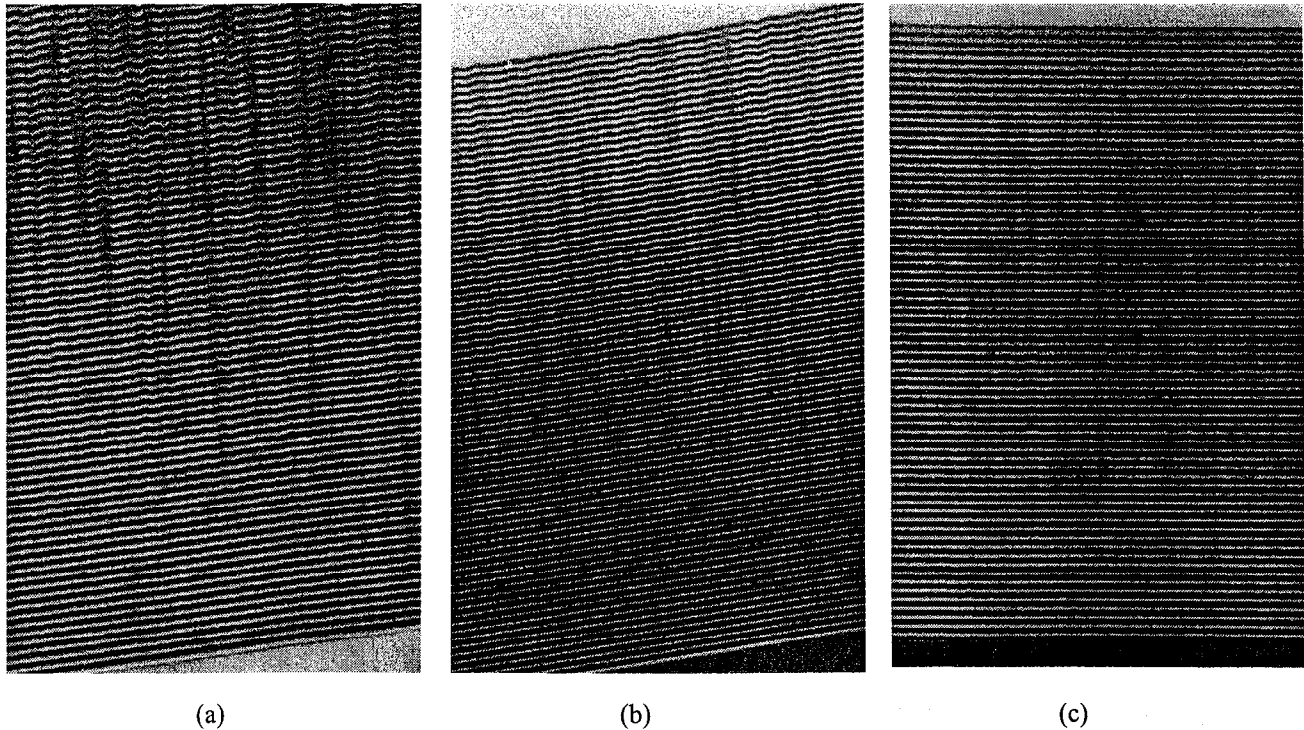


Figure 5: Cross section TEM images of Mo/Be multilayers deposited at different Ar sputtering pressures: 2.5 mTorr (a), 1.7 mTorr (b), and 0.8 mTorr (c)

observed in the experiments. Indeed, we found that the optimum number of bilayers is 70 for Mo/Be and Mo₂C/Be multilayer coatings, while it is only 50 for Ru/Be multilayer coatings.

Roughness of the multilayer is strongly connected to the crystalline structure of the materials used. For example, polycrystalline films are much rougher than amorphous ones. Figures 6(a)-(c) display cross section images of the three multilayer systems. The contrast of these images is due to different transmission of electrons in different materials. Darker color is associated with lower transmission and hence with higher Z material. For example, in Mo/Be multilayer the dark bands are due to Mo and the light bands are due to Be. A high resolution TEM image of Mo/Be (Fig. 6a) reveals that both Mo and Be are deposited as polycrystalline materials. In an earlier paper,² polycrystalline Mo and amorphous Be were observed in Mo/Be multilayers deposited by DC magnetron sputtering. The crystalline structure of Mo in our films is bcc and the crystallites have predominantly a $\langle 110 \rangle$ orientation in the growth direction. However, beryllium in our films has hcp crystalline structure and $\langle 0110 \rangle$ texture. The resolvable lattice spacing of the Be crystallites is around 0.17 nm, which approaches the TEM resolution. The texture in Be layers is not well developed and extremely thin areas are covered with the surface oxide that obscures imaging bulk Be. However, electron diffraction confirms that Be is indeed crystalline.

Figure 6c shows a TEM image of a Mo₂C/Be multilayer. This multilayer has sharper interfaces than Mo/Be multilayers. Furthermore, these interfaces also appear smoother. Beryllium layers are still polycrystalline with an hcp structure but the Mo₂C layers are amorphous. The amorphous Mo₂C layers provide a smoothing mechanism that reduces the roughness caused by the crystalline layers of Be. In this respect this multilayer is very similar to the Mo/Si multilayer system where Mo is crystalline and Si is amorphous.¹⁰⁻¹²

Another important parameter that modifies the roughness of the multilayer is the roughness of the substrate. An atomic force microscope (AFM) was used to measure the high frequency roughness of the substrates and correlate it with the roughness of the deposited Mo/Be films. These measurements were done using a commercial Nanoscope III AFM with the following components: Nanoscope III controller with phase extender box, dimension 3000 AFM with type G scanner and with a standard silicon tip. The field size was 2 x 2 μm and the substrate roughness was measured before the deposition and the multilayer top surface was measured after the deposition. Figure 7 displays the substrate roughness vs. the Mo/Be multilayer roughness. The substrate was Zerodur, which is a glass ceramic specifically designed to have a low thermal expansion coefficient. A comparison between Mo/Be and Mo/Si multilayer coatings on Zerodur substrates can be found in Mirkarimi *et al.*¹³ A multilayer has a smoothing effect on the substrate roughness if the roughness of the multilayer approaches the roughness of the substrate or gets even lower than the roughness of the substrate. Such a trend was observed

in Mo/Si multilayers¹³. With Mo/Be multilayers however, the roughness of the multilayer is always higher than the substrate roughness and it increases with higher substrate roughness as shown in Fig. 7.

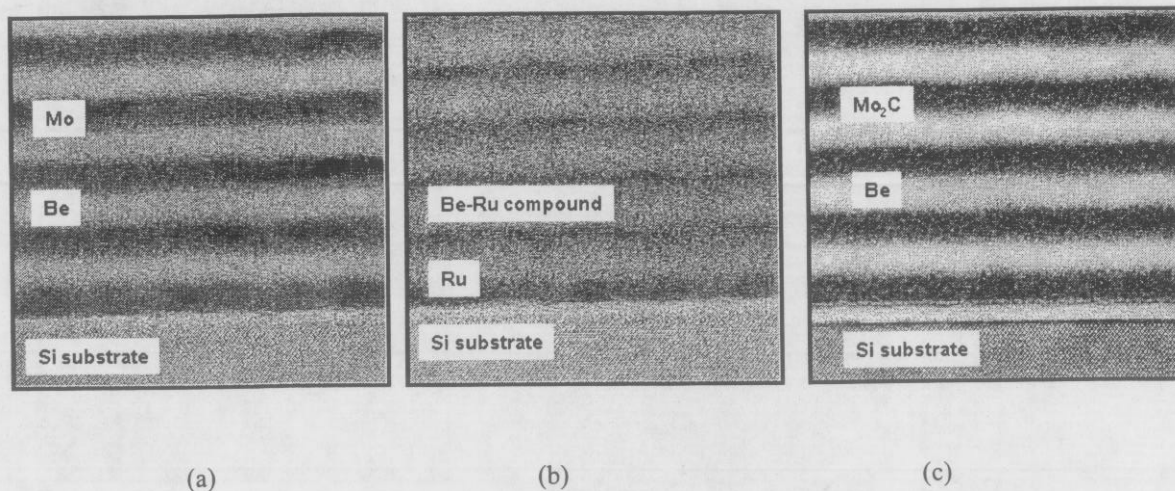


Figure 6: Cross section TEM images of Mo/Be (a), Ru/Be(b) and Mo₂C/Be (c) multilayers.

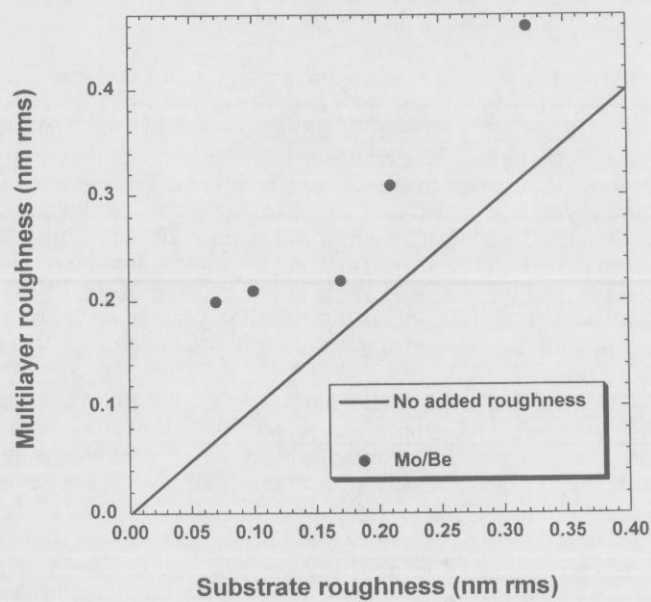


Figure 7: AFM measurements of the Zerodur substrate roughness (before) and the roughness of the Mo/Be multilayer coating (after).

3.1.2 Interlayer mixing

Multilayer reflectance can be different than predicted due to interlayer mixing. The interfaces in our Mo/Be multilayers are rather sharp. Nevertheless, we can still resolve thin, asymmetric interlayers of mixed composition at the layer boundaries. We estimate that the Be-on-Mo interface is slightly thinner (0.2-0.3 nm) than the Mo-on-Be interface (0.6-0.8 nm). A phase diagram¹⁴ of MoBe compounds shows three possible compositions that form at room temperature and under equilibrium conditions: Be_{12}Mo , Be_2Mo and BeMo_3 . Unfortunately, these interfaces are too narrow for analytical measurements and so we were not able to determine which MoBe compounds form at these interfaces. The difference in calculated and measured reflectivity in Mo/Be multilayers can be ascribed to the oxidation of the surface, slight interlayer mixing at the interfaces, and to the interlayer roughness.

The TEM image of a cross section of a Ru/Be multilayer is shown in Fig. 6b. This multilayer system suffers from an extensive interlayer mixing between Ru and Be layers. In fact, no evidence of pure Be could be found in the electron diffraction pattern. It appears that all Be is consumed to form a Ru-Be compound, while some pure Ru is still present in the multilayer. This Ru layer has a hcp crystalline structure. The significant disagreement between the calculated and measured reflectivity shown in Fig. 3, can be attributed to the surface oxidation and to the reaction of the Be and Ru layers, which lowers the optical contrast of the multilayer interfaces.

Auger analysis of $\text{Mo}_2\text{C}/\text{Be}$ multilayers suggests the presence of a few atomic % of oxygen in the Mo_2C layers. This is probably due to oxygen impurities in the sputter target. In addition to surface oxidation, this seems to be a major cause for the reflectance loss in this multilayer.

3.1.3 Surface oxidation

All three multilayer systems suffered a loss in reflectance caused by surface oxidation. Surface oxidation was determined by x-ray photoemission spectroscopy (XPS) and observed in high resolution TEM images. Beryllium forms a 3-4 nm thick BeO which can be seen in Fig. 8. The multilayers were usually capped with Be because BeO seems to be more stable than Mo oxides or Ru oxides. If the multilayer is capped with Mo or Ru, for example, the reflectance is up to 4% lower as compared to a Be capped multilayer. Similar observations were made previously¹.

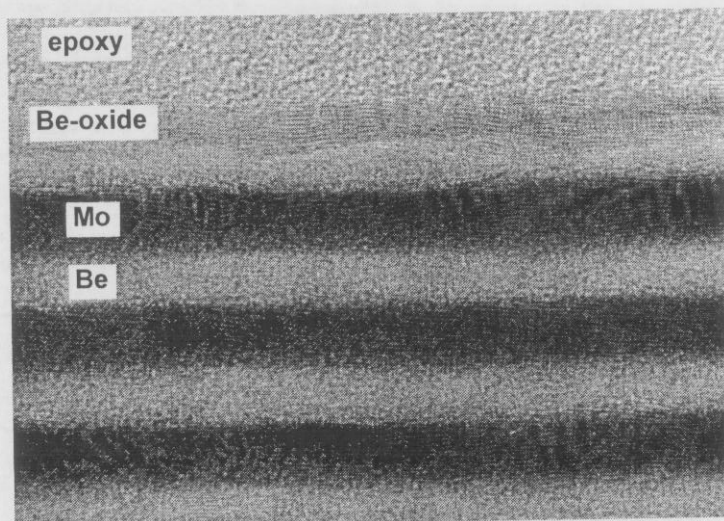


Figure 8: TEM cross section image of Mo/Be multilayer showing a few top layers with crystalline Be-oxide as the terminating layer.

Finding an appropriate capping material can help reduce surface oxidation. Table 1 lists the results of an experiment on $\text{Mo}_2\text{C}/\text{Be}$ multilayers capped with different materials. The reflectance was measured soon after the deposition of the multilayers. The beryllium capped multilayer has a higher reflectance than the Mo_2C capped one. However, the best reflectance is achieved by capping the Mo_2C layer with an additional 0.2 nm carbon layer.

Capping material	Reflectance (%)
Be	61.38
Mo ₂ C	58.28
0.2 nm C on Mo ₂ C	64.41

Table 1: Reflectance results for Mo₂C/Be multilayers capped with different materials.

3.2 Stress

Stringent figure requirements for the coated optics in an EUV projection lithography system require minimizing deformation due to the multilayer film stress. Several ways to minimize intrinsic stress of Mo/Si and Mo/Be have been proposed.¹⁵⁻¹⁶ In Table 2 we list the stress values for each multilayer system together with the thickness of each multilayer.

Multilayer	Stress (MPa)	Thickness (nm)
Mo/Be	+330 (tensile)	404
Ru/Be	-410 (compressive)	293
Mo ₂ C/Be	+88 (tensile)	402

Table 2: Intrinsic stress and thickness for the three multilayer systems

Film stress in our Mo/Be multilayers was measured to be tensile and +330 MPa. The Mo layers are in tension and the Be layers are in compression. The Mo/Be films are thicker than Mo/Si films and would therefore induce more curvature to the optic. It has also been demonstrated that thermal annealing, which is often used to reduce the stress in multilayers, would actually increase the stress in Mo/Be multilayers. Therefore an alternative and innovative approach was developed to reduce intrinsic stress in Mo/Be multilayers. A buffer-layer of amorphous Si, which is compressive, deposited directly on the substrate (below the multilayer) compensates the intrinsic stress of Mo/Be multilayers to near zero with less than 1% reduction in reflectance.¹⁵⁻¹⁶

Both Mo/Be and Ru/Be multilayer films have high intrinsic stress. The intrinsic stress of Ru/Be is -410 MPa. The values in Table 2 show that Mo₂C/Be, on the other hand, is a low stress multilayer. We measured only +88 MPa in a typical Mo₂C/Be multilayer.

3.3 Reflectance stability

3.3.1 Reflectance stability under atmospheric conditions

We monitored the reflectance change of Mo/Be multilayers stored at room temperature in ambient air. An absolute reflectance loss of up to 2% was measured on Mo/Be multilayers capped with Be that were 20 months old. The absolute reflectance drop in Mo/Be multilayers capped with Mo was on average 2.8% for 22 months old multilayers. Nevertheless, the reflectance wavelength and the peak bandwidth changed by less than 0.03 nm.

Ru/Be multilayers are not as stable as Mo/Be multilayers. In an 8 month old sample, for example, we measured an absolute reflectance drop of 3%. The reflectance wavelength and the peak bandwidth changed as well. The peak wavelength shifted to a shorter wavelength by 0.04 nm and the peak bandwidth shrank by 0.02 nm. For a comparison, no change in reflectance wavelength or peak bandwidth was observed in Mo/Be coatings of the same age. Based on theoretical simulations we find that the most probable reason for the continuing reflectance drop, reflectance wavelength shift and peak bandwidth reduction is due to progressive interlayer mixing and surface oxidation.

Two Mo₂C/Be multilayers made during the same deposition run were monitored for the reflectance and wavelength change. One multilayer was capped with Mo₂C and the other with an additional 0.2 nm of carbon on the top of Mo₂C layer. The reflectance of these two multilayers was measured after the deposition (Table 2) and again after 10 months. An absolute

reflectance drop of 3.5% was observed in Mo₂C capped multilayer. However, an additional 0.2 nm of carbon stabilized the reflectance of Mo₂C/Be multilayer. A ten month old sample lost only 0.7% in absolute reflectance. The reflectance wavelength shifted to a shorter wavelength by 0.03 nm yet the peak bandwidth remained unchanged.

3.3.2 Rapid thermal annealing

In EUV lithography, reflective masks will be made by patterning an absorber on top of a multilayer-coated substrate. During the EUV mask processing the coating has to undergo many chemical and thermal cycles. The risk of exposing the reflective coatings to high temperatures, even for relatively short times, has to be assessed. In this section we present results obtained on Mo/Be multilayers exposed to rapid thermal annealing.

The rapid thermal annealing experiments were performed at LLNL using a AET-ADDAX Rapid Thermal Processor RX from Tencor. A single 101 mm diameter Si (100) wafer coated with a Mo/Be multilayer was cut into several 25 x 25 mm pieces. Since our sputter deposition sources produce extremely uniform coatings (thickness uniformity better than 0.1% over a 110 mm diameter wafer) we assumed that all the pieces have initially the same reflectance. This assumption proved valid for other multilayers deposited on 101 mm diameter Si wafers. One piece was placed on a bare supporting Si wafer. Thermal annealing was achieved by infrared radiation produced from a row of quartz lamps underneath the supporting wafer. Two thermocouples were attached to the supporting wafer and to the Mo/Be piece sitting on the top of the wafer. The thermocouples attached to the Mo/Be piece consistently measured a few degrees lower temperature than the thermocouples attached to the supporting Si wafer. Table 4 lists the temperatures measured on the Mo/Be samples.

The process chamber with the sample was filled with Ar and left at room temperature for about 30 seconds. The temperature was then raised to its maximum target temperature in 30 seconds, maintained constant at the maximum temperature for 30 seconds and finally cooled down to room temperature. Since no active cooling was used this last part usually took up to 3 minutes. The Mo/Be multilayer coatings were annealed to temperatures between 82 and 343 °C. One of the samples was not annealed and served as a reference sample. After the annealing the reflectivities of the samples were measured and the values are listed in Fig. 9. No change in reflectance was detected for the samples heated between 82 and 239 °C. However, absolute reflectance losses of 0.7% and 1.5% were detected at 293 °C and at 343 °C, respectively. It is interesting that this reflectance loss is smaller than that observed in a typical Mo/Si multilayer. For example, the reflectance loss in a Mo/Si multilayer that was annealed to 300°C is about 2%. If annealed to 400°C this reflectance loss becomes even more dramatic and reaches 7%.¹⁷

The reflectance loss in multilayers due to thermal annealing is often connected to the change in the reflectance peak wavelength. Usually the period thickness shrinks which causes the peak wavelength to shift towards shorter wavelengths. In Mo/Be, however, the peak wavelength remained constant for all annealed samples suggesting that the period thickness of these multilayers remained unchanged, at least up to 350°C. Nevertheless we noticed a change in bandwidth which gets narrower with the increasing annealing temperature (Fig. 9). For example, the peak width shrank by 2% (relative) at 187°C and a change up to 10% was measured at 343°C. A narrower peak width suggests progressive mixing at the interfaces, which reduces the reflectance as shown in Fig. 9.

3.3.3 EUV radiation exposure

The lifetime of an EUVL optical system depends critically on the stability of the reflective multilayer coatings under EUV radiation exposure. Therefore it is necessary to assess the effects of EUV exposure on Mo/Be multilayers. Intense radiation from the undulator beamline 12.0.1 at the ALS¹⁸ was used to study the radiation effects on Mo/Be multilayer mirrors. The intensities were much higher than the intensities expected in an EUVL optical system, which enabled us to accelerate the experiments. The exposed area (10⁻³ cm²) on the coating received about 10 W/cm² of the radiation. This corresponds to a radiation dose of 1.72 J/cm². Mo/Be multilayers were exposed to EUV radiation in a vacuum chamber with a base pressure of 10⁻⁹ Torr. The average power of EUV radiation was 35mW and the exposure time was about 40 hours. After the exposure the samples were examined visibly and by Auger electron spectroscopy for any changes of the surface. More details about this study and the experimental setup can be found in Wedowski *et al.*¹⁹

The reflectance in the exposed area was measured with the EUV reflectometer on beamline 6.3.2 at the ALS. The reflectance in the exposed area dropped from 66.5% to 64.5% (a reflectance loss of 2%) however no change in peak wavelength or peak bandwidth was detected. About 1% of the reflectance loss could be recovered by ozone cleaning¹⁹.

It appears that the top Be layer on the surface of the Mo/Be multilayer oxidizes upon exposure to air even without radiation exposure. The thickness of such oxide typically reaches 3-4 nm. After the EUV exposure a thin layer of carbon was found covering the area exposed to EUV radiation. This contamination is what caused the 2% reflectance drop, and is most probably due to hydrocarbons still present in the vacuum chamber. However, after cleaning with ozone, Auger electron spectroscopy showed that all traces of carbon had been removed. Nevertheless, the reflectance of the exposed area remained

1% lower than the surrounding area. Auger spectroscopy data show that beryllium-oxide layer got thicker during the cleaning with the ozone. An increase of 0.3-0.4 nm in the thickness of BeO layer is sufficient to explain the 1% reflectance loss in Mo/Be multilayer.

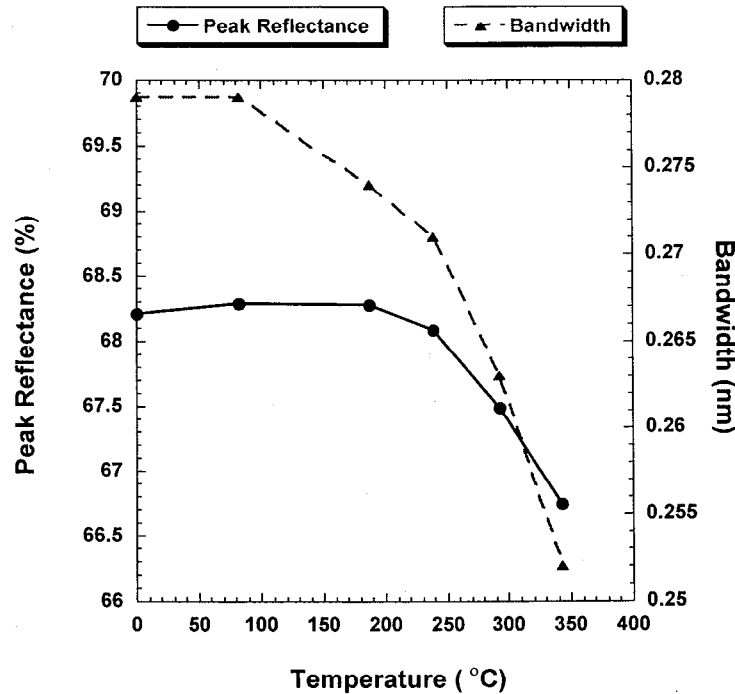


Figure 9: Reflectance and bandwidth values of Mo/Be samples after rapid thermal annealing experiment.

3.4 Stress stability

Data on stress stability are still very limited. Here we present data on Mo/Be multilayer stress for a time period of about 11 months. Intrinsic stress, which was originally $+335 \pm 5$ MPa (tensile) changed on average only by 1% over the first 11 months. In contrast, stress changes of up to 13% over the same period of time were observed in Mo/Si multilayers.¹⁶

4. SUMMARY

Three beryllium-based multilayer coatings, Mo/Be, Ru/Be and Mo₂C/Be, were studied and compared for their reflectance, stress, and reflectance and stress stability. Mo/Be mirrors consistently give the highest reflectances among the three multilayer mirrors but only when the substrate is extremely smooth (better than 0.1 nm rms). Indeed, the reflectance of the Mo/Be multilayer system strongly depends on the substrate roughness because both Mo and Be layers are polycrystalline. The Mo₂C/Be mirrors are intrinsically smoother because Mo₂C forms amorphous layers. It also has the advantage of very low intrinsic stress. A higher purity sputtering target might produce higher reflectance Mo₂C/Be multilayers. More studies are needed to evaluate the thermal and radiation stability of Ru/Be and Mo₂C/Be multilayer mirrors. Theoretically the Ru/Be mirrors should have the highest reflectance and the largest bandwidth and seemed to be the best candidate for EUVL reflective coatings at 11 nm. However, multilayer mirrors made of this material pair do not perform very well. Strong intermixing between Be and Ru lowers the optical contrast of the interfaces. Continuous reduction of the peak reflectance and bandwidth suggests that the mixing is progressive and that these mirrors are not stable even at room temperature. This problem could be solved by using a thin layer of a third material that would serve as a diffusion barrier between Ru and Be.

In order to use beryllium-based multilayer coatings for EUVL production tools these mirrors have to satisfy many requirements. Among them are high reflectance, low stress, low roughness and good thermal and radiation stability. To date, no beryllium-based multilayer system has met all of those criteria simultaneously. More research is necessary to find the ideal candidate that will satisfy all these requirements.

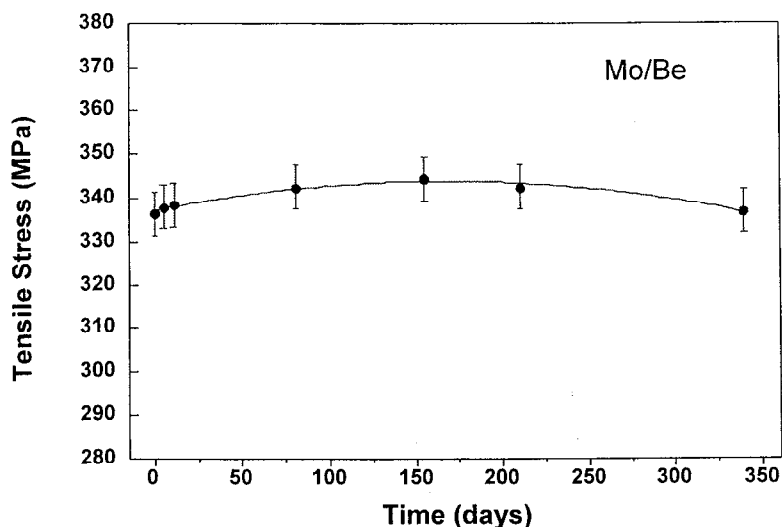


Figure 8: Stress stability of Mo/Be multilayers

5. ACKNOWLEDGMENTS

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6. REFERENCES

1. K. M. Skulina, C. S. Alford, R. M. Bionta, D. M. Makowiecki, E. M. Gullikson, R. Soufli, J. B. Kortright, and J. H. Underwood, "Molybdenum/beryllium multilayer mirrors for normal incidence in the extreme ultraviolet," *Appl. Opt.* **34**, 3727-3730 (1995).
2. D. G. Stearns, K. M. Skulina, C. S. Alford, R. M. Bionta, D. M. Makowiecki, E. M. Gullikson, R. Soufli, J. B. Kortright, and J. H. Underwood, "Beryllium-based multilayer structures," *Mat. Res. Soc. Symp. Proc.*, Vol. **382**, 32-336, Materials Research Society (1995).
3. C. Montcalm, S. Bajt, P. B. Mirkarimi, F. J. Weber, and J. A. Folta, "Multilayer reflective coatings for extreme-ultraviolet lithography," in *Emerging Lithographic Technologies II*, Y. Vladimirsky, Ed., Proceedings of SPIE Vol. **3331**, 42-51 (1998).
4. All theoretical calculations were done using D. Windt's program IMD, which can be downloaded from <http://www.bell-labs.com/user/windt/idl/>.
5. G. D. Kubiak, L. J. Bernardez, K. Krenz, "High-power extreme ultraviolet source based on gas jets", in *Emerging Lithographic Technologies III*, Y. Vladimirsky, Ed., Proceedings of SPIE Vol. **3331**, 81-88 (1998).
6. G. D. Kubiak, L. J. Bernadez, K. Krenz, W. C. Sweatt, "Scale-up of a cluster jet plasma source for extreme ultraviolet lithography" in *Emerging Lithographic Technologies III*, Y. Vladimirsky, Ed., Proceedings of SPIE Vol. **3676**, 669-678 (1999).
7. D. W. Sweeney, R. M. Hudyma, H. N. Chapman, "EUV optical design for 100-nm CD imaging system", in *Emerging Lithographic Technologies III*, Y. Vladimirsky, Ed., Proceedings of SPIE Vol. **3331**, 2-10 (1998).

8. J.H. Underwood and E.M. Gullikson, "High-resolution, high-flux, user friendly VLS beamline at the ALS for the 50-1300 eV energy region", *J. Elect. Spect. and Rel. Phen.* **92**, 265-272 (1998).
9. R. Soufli, S. Bajt, E. M. Gullikson, "Optical constants of beryllium from photoabsorption measurements for multilayer optics applications", in this Proceedings.
10. D. G. Stearns, R. S. Rosen, S. P. Vernon, "Fabrication of high-reflectance Mo-Si multilayer mirrors by planar-magnetron sputtering", *J. Vac. Sci. Technol.* **A9**, 2662-2669 (1991).
11. Y. Cheng, D. J. Smith, M. B. Stearns, and D. G. Stearns, "Optimization of growth conditions of vapor deposited Mo/Si multilayers", *J. Appl. Phys.* **72**, 5165-5171 (1992).
12. D. G. Stearns, R. S. Rosen, and S. P. Vernon, "Multilayer mirror technology for soft x-ray projection lithography", *Appl. Opt.* **32**, 6952-6960 (1993).
13. P. B. Mirkarimi, S. Bajt, M. A. Wall, "Mo/Be and Mo/Si multilayer coatings on Zerodur substrates for extreme ultraviolet lithography", submitted to Applied Optics.
14. H. Okamoto, L. E. Tanner, "The Be-Mo (beryllium-molybdenum) system", preprint, UCRL-94477 (1986).
15. P. B. Mirkarimi, and C. Montcalm, "Advances in the reduction and compensation of film stress in high-reflectance multilayer coatings for extreme ultraviolet lithography", in *Emerging Lithographic Technologies II*, Y. Vladimirski Ed., Proceedings of SPIE Vol. **3331**, 133-148 (1998).
16. P. B. Mirkarimi, "Stress, reflectance and temporal stability of sputter-deposited Mo/Si and Mo/Be multilayer films for extreme ultraviolet lithography", *Opt. Eng.* **38**, 1246-1259 (1999).
17. C. Montcalm, paper in preparation.
18. D. Attwood, G. Sommargren, R. Beguiristain, "Undulator radiation for at-wavelength interferometry of optics for extreme-ultraviolet lithography", *Appl. Opt.* **32**, 7022-7031 (1993).
19. M. Wedowski, S. Bajt, J. A. Folta, E. M. Gullikson, U. Kleineberg, L. E. Klebanoff, M. E. Malinowski, W. M. Clift, "Lifetime studies of Mo/Si and Mo/Be multilayer coatings for extreme ultraviolet lithography", in this Proceedings.